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Multimetallic complexes based on a diphosphine-dithiocarbamate 'Janus' ligand.

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Supporting Information (consisting of crystallographic data and anisotropic displacement ellipsoid plots for the structures of **5** and **9**) are available on the WWW under http://.

Keywords: ruthenium, dithiocarbamate, sulfur ligands, multimetallic

Abstract

The aminodiphosphine ligand, $HN(CH_2CH_2PPh_2)_2$, reacts with $[M(CO)_4(pip)_2]$ (M = Mo, W; pip = piperidine) to yield $[M\{\kappa^2\text{-}HN(CH_2CH_2PPh_2)_2\}(CO)_4]$. The molybdenum analogue readily loses a carbonyl ligand to form $[Mo\{\kappa^3\text{-}HN(CH_2CH_2PPh_2)_2\}(CO)_3]$, which was structurally characterized. The same ligand backbone is used to form the new bifunctional ligand, $KS_2CN(CH_2CH_2PPh_2)_2$, which reacts with nickel and cobalt precursors to yield $[Ni\{S_2CN(CH_2CH_2PPh_2)_2\}_2]$ and $[Co\{S_2CN(CH_2CH_2PPh_2)_2\}_3]$. Addition of [AuCl(tht)] (tht = tetrahydrothiophene) to $[Ni\{S_2CN(CH_2CH_2PPh_2)_2\}_2]$ leads to formation of the pentametallic complex, $[Ni\{S_2CN(CH_2CH_2PPh_2AuCl)_2\}_2]$. In contrast, addition of $[PdCl_2(py)_2]$ (py = pyridine) to $[Ni\{S_2CN(CH_2CH_2PPh_2)_2\}_2]$ does not lead to a trimetallic complex but instead yields the cyclic bimetallic compound $[Pd\{S_2CN(CH_2CH_2PPh_2)_2\}]_2$, which was structurally characterized. The same product is obtained directly from $[PdCl_2(py)_2]$ and $KS_2CN(CH_2CH_2PPh_2)_2$. In contrast, the same reaction with $[PtCl_2(NCPh)_2]$ yields the polymer, $[Pt\{S_2CN(CH_2CH_2PPh_2)_2\}]_n$. Reaction of $KS_2CN(CH_2CH_2PPh_2)_2$ with cis-$[RuCl_2(dppm)_2]$ provides $[Ru\{S_2CN(CH_2CH_2PPh_2)_2\}(dppm)_2]^+$, which reacts with [AuCl(tht)] to yield $[Ru\{S_2CN(CH_2CH_2PPh_2AuCl)_2\}(dppm)_2]^+$. Addition of $[M(CO)_4(pip)_2]$ (M = Mo, W) to the same precursor leads to formation of the bimetallic compounds $[(dppm)_2Ru\{S_2CN(CH_2CH_2PPh_2)_2\}M(CO)_4]^+$, while treatment with $[ReCl(CO)_5]$ yields $[(dppm)_2Ru\{S_2CN(CH_2CH_2PPh_2)_2\}ReCl(CO)_3]^+$. Reaction of $KS_2CN(CH_2CH_2PPh_2)_2$ with $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ (BTD = 2,1,3-bezothiadiazole) provides $[Os(CH{=}CHC_6H_4Me\text{-}4)\{S_2CN(CH_2CH_2PPh_2)_2\}(CO)(PPh_3)_2]$, but reaction with the analogous ruthenium precursor fails to yield a clean product.

Introduction

Alongside thiolate compounds, dithiocarbamate complexes, MS_2CNR_2, feature at the forefront of S-ligand transition metal coordination chemistry. In the hundred years since the first report of a transition metal bearing the dithiocarbamate ligand,[1] a vast array of examples has been reported,[2] Although significant advances have been achieved in recent years,[2e,3] this versatility has often been left unexploited in terms of extending the ligand architecture beyond simple nitrogen substituents (R = Me, Et are commercially available).

Our recent contributions in the area of multimetallic assembly[4-6] have attempted to tap this potential in studies exploring the possibilities offered by manipulation of the NR_2 substituents (e.g., coordination to other metals,[4] alkene metathesis,[7]) as well as addressing applications such as d-f hybrids with potential for medical imaging.[8] For over a decade, renewed interest in dithiocarbamates has also focused on their use as surface units for capping gold nanoparticles.[5,7c,8-10] Linked to this development, a number of reports have probed the potential of this method for placing metal units on the surface of gold nanoparticles.[5,8,10]

Bifunctional linkers bearing dithiocarbamates have been employed in both multimetallic assemblies and metal-functionalized nanoparticles. Examples with additional dithiocarbamate,[5,11] bipyridine,[10a] terpyridine[10b] and porphyrin[10c] units have been demonstrated to allow incorporation of additional metal units beyond the dithiocarbamate unit itself. This can be achieved through generation of the second donor site after attachment of the first metal, as shown in the treatment of $[Ru(S_2CNC_4H_8NH_2)(dppm)_2]$ with base, carbon disulfide and a metal to provide $[Ru(S_2CNC_4H_8NCS_2ML_n)(dppm)_2]^{m+}$.[4a,b,5a] Alternatively, addition of further metals to the system can be achieved through the preference of the new metal (e.g., lanthanide ions) for the harder oxygen and nitrogen donors of a macrocycle.[8]

While bifunctional phosphine-thiol linkers have been used successfully to modify the surface of nanoparticles,[12,13] to our knowledge, no linker has been reported which bears both dithiocarbamate and phosphine functionalities. Given the ubiquity of phosphine ligands in applications of transition metals, this linker was considered a very promising route to multimetallic complexes with potential for roles in homogeneous catalysis. As described below, while this route was successful in a number of cases, unexpected coordination chemistry can also occur. In discussing this reactivity, it is useful to draw upon the analogous amino-functionalized complexes reported in 2009 (Fig. 1)[4f] and amine-phosphine complexes based on the same $RN(CH_2CH_2PPh_2)_2$ backbone (*vide infra*).

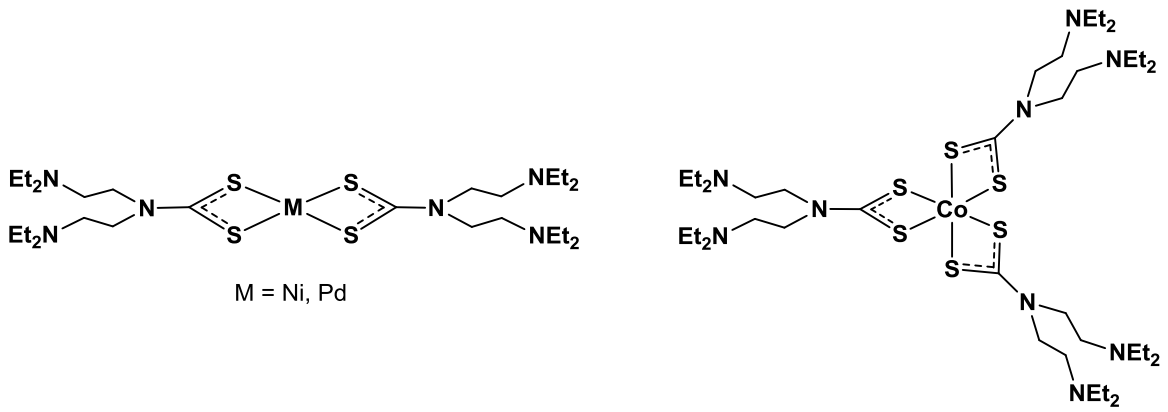


Figure 1. Examples of amine-terminated dithiocarbamate complexes.

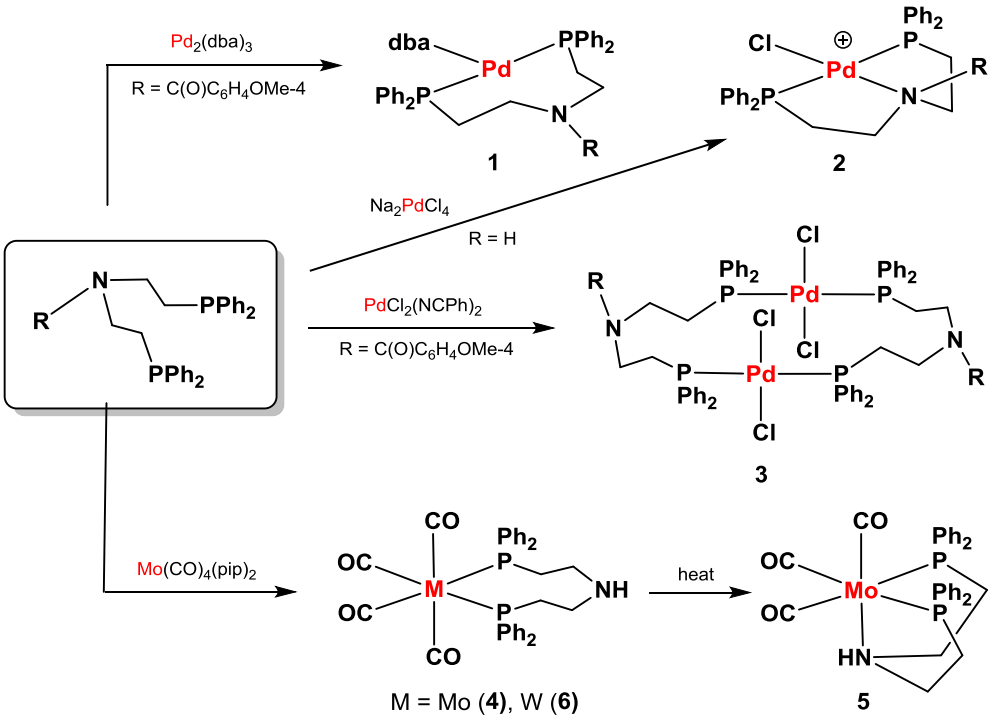
Results and Discussion

Preparation of amino-diphosphine compounds

Chelates combining phosphine and amine (or amide) donors have been used widely in transition metal chemistry and have found particularly frequent application in catalysis.[14] Ligands of the type, $RN(CH_2CH_2PPh_2)_2$, show a range of coordination modes, which illustrate the flexibility of the ethylene bridges (Scheme 1). Bis[2-(diphenylphosphino)ethyl]amine is readily accessible from commercially available bis(2-chloroethyl)amine and diphenylphosphine in the presence of KO^tBu. Acid work-up is also often employed to furnish the hydrochloride salt,[15] which is a convenient starting point for further functionalisation.[16]

With zerovalent palladium precursors such as $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone), bidentate diphosphine chelates are observed (**1**), which are in equilibrium with the tridentate PNP donor combination in coordinating solvents.[16] With Pd(II) precursors, cationic complexes are isolated (**2**)[16] in which the phosphine ligands have been crystallographically determined to adopt a *trans* arrangement.[17] A different, cyclic coordination mode (**3**) is observed on reaction of equimolar amounts of the diphosphine ligand and $[PdCl_2(NCMe)_2]$.

In order to explore the coordination possibilities of this framework further and to establish the availability of the nitrogen unit for further functionalization, a series of molybdenum complexes was investigated (Scheme 1).



Scheme 1. Reactivity of the aminophosphine backbone used in this work; dba = dibenzylideneacetone; pip = piperidine.

Treatment of the versatile zerovalent molybdenum precursor, $[Mo(CO)_4(pip)_2]$ (pip = piperidine) with one equivalent of $HN(CH_2CH_2PPh_2)_2$ led initially to bidentate coordination through the phosphines. The product was formulated as the tetracarbonyl species, $[Mo\{\kappa^2\text{-}HN(CH_2CH_2PPh_2)_2\}(CO)_4]$ (**4**), on the basis of the solid state infrared spectrum (four absorptions between 1862 – 2013 cm^{-1}) and a molecular ion in the mass spectrum at *m/z* 650. In addition to a singlet in the $^{31}P\{^1H\}$ NMR spectrum at 19.8 ppm, ^1H NMR analysis revealed resonances for the ethylene bridges at 1.66 and 2.71 ppm.

Although some spectroscopic data could be obtained, isolating **4** proved to be challenging as spontaneous loss of a carbonyl ligand was found to occur even under mild conditions, leading to coordination of the nitrogen donor to give the tricarbonyl product $[Mo\{\kappa^3\text{-}HN(CH_2CH_2PPh_2)_2\}(CO)_3]$ (**5**). The features displayed in the ^1H NMR spectrum did not change substantially, however, a simplification of the absorptions in the infrared spectrum was observed and a new resonance was noted in the $^{31}P\{^1H\}$ NMR spectrum at 39.2 ppm. This complex has been reported previously by Ellermann and coworkers, whose data are in good agreement with those obtained in this work.[18] In order to provide structural data and to

investigate the flexibility of the phosphine arms of the chelate, single crystals of **5** were successfully grown and a structural study undertaken (Fig. 2).

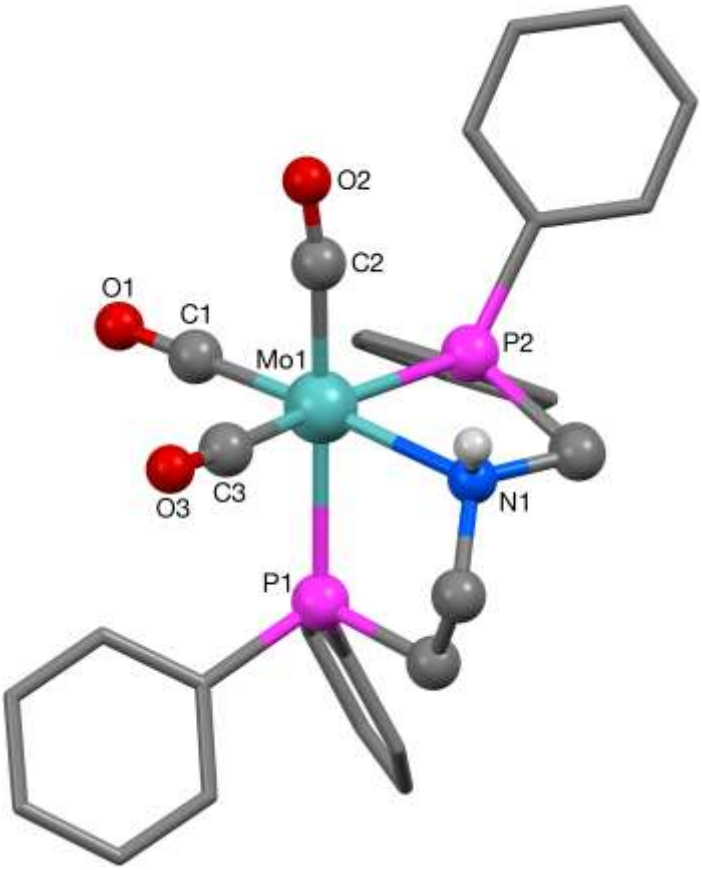


Figure 2. The molecular structure of [Mo{κ^3-HN($CH_2CH_2PPh_2$)$_2$}$(CO)_3$] (**5**). Selected bond lengths (Å) and angles (°): Mo(1)–C(1) = 1.9491(15), Mo(1)–C(3) = 1.9497(15), Mo(1)–C(2) = 1.9772(15), Mo(1)–N(1) = 2.3340(12), Mo(1)–P(2) = 2.5292(4), Mo(1)–P(1) = 2.5400(4), O(1)–C(1) = 1.1635(19), O(2)–C(2) = 1.1580(19), O(3)–C(3) = 1.1680(18), C(1)–Mo(1)–N(1) = 174.97(5), N(1)–Mo(1)–P(1) = 77.22(3), N(1)–Mo(1)–P(2) = 78.31(3), C(1)–Mo(1)–P(2) = 100.19(5).

The complex adopts a distorted octahedral structure with *cis*-interligand angles in the range 77.22(3) – 100.19(5)°. The P-N-P ligand is chelated in a *facial* manner through five-membered metallacycles, in which some degree of strain is evident, with the smallest angles between *cis* donors being the N–Mo–P angles. The facial coordination in this complex was inferred previously from spectroscopic data, in contrast to the chromium analogue which is thought to adopt a *mer*-arrangement.[18] Ellermann and co-workers also proposed interactions

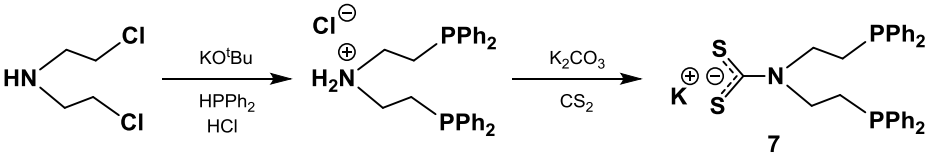
between the carbonyl ligands and the *ortho*-protons of the phenyl rings (in line with their previous work[19]). In the structure of **5**, the PNP ligand adopts a low symmetry arrangement such that the closest C-O approach to an *ortho*-phenyl proton attached to the P2 phosphorus is around 2.80 Å whereas the closest interaction involving the protons of the aryl substituents attached to P1 is approximately 3.00 Å. In both cases the C-H…O hydrogen bonding interactions deviate substantially from the usual 180° angle, displaying angles of 123° and 106° for the interactions involving the substituents on the P2 and P1 atoms, respectively. More substantial interactions are observed between the N-H hydrogen and oxygen atoms in neighboring molecules. These are linked through the N-H hydrogen and the O3 carbonyl oxygen atom in a C_i related molecule (and vice versa) forming a dimer pair [the N…O distance is 3.085 Å and the H…O distance is 2.29 Å with the N-H angle of 148° and the bond distance set at 0.9 Å].

The tungsten analogue, $[W\{\kappa^2\text{-}HN(CH_2CH_2PPh_2)_2\}(CO)_4]$ (**6**), was also prepared by the same route from $[W(CO)_4(pip)_2]$. Similar spectroscopic data were observed for this compound as for **4**, apart from the presence of tungsten satellites (J_{PW} = 234.0 Hz) in the $^{31}P\{^1H\}$ NMR spectrum for the resonance at 2.9 ppm. The formulation was further supported by good agreement of elemental analysis with calculated values and a molecular ion in the mass spectrum at *m/z* 738. The tungsten analogue of **5**, $[W\{\kappa^3\text{-}HN(CH_2CH_2PPh_2)_2\}(CO)_3]$, is known, although prepared by a different route.[18] However, in contrast to the reaction shown by **4**, compound **6** showed no tendency to form this tricarbonyl product, allowing the reactivity of the pendant amine to be explored as an alternative route to multimetallic complexes.

Taken together, the structural diversity of these compounds established the reactivity of the phosphine donors and that of the bridgehead nitrogen in the $HN(CH_2CH_2PPh_2)_2$ ligand. The effect of transforming the nitrogen into a dithiocarbamate to provide a sulfur-phosphine donor combination in place of the PNP arrangement was then investigated.

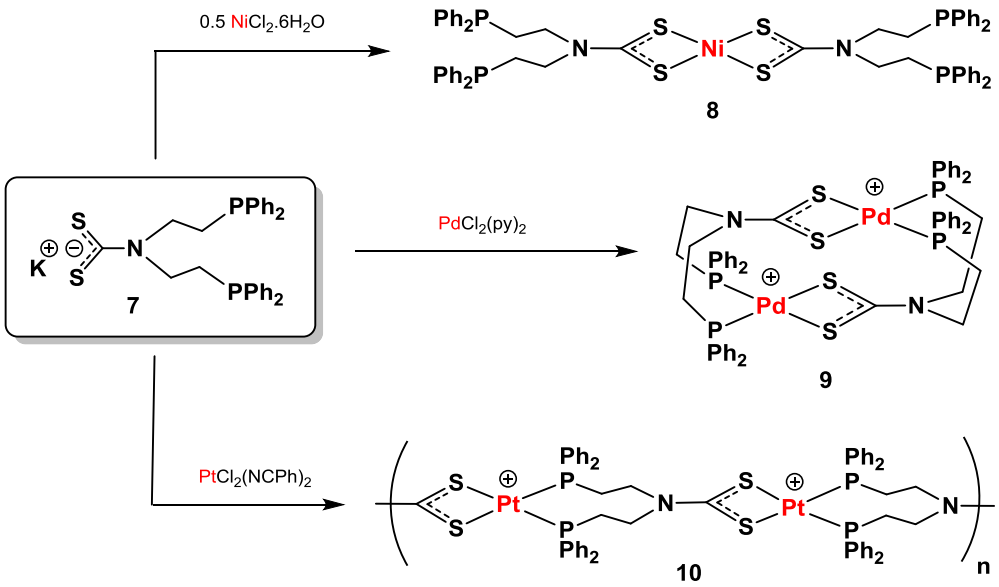
Synthesis of homonuclear dithiocarbamate complexes

Various bases (KOH, NEt_3, DBU) were explored for the deprotonation of the hydrochloride salt, $[H_2N(CH_2CH_2PPh_2)_2]Cl$, however, potassium carbonate in dry acetonitrile was found to be most effective, leading to isolation of $KS_2CN(CH_2CH_2PPh_2)_2$ (**7**) in 91% yield. A new singlet was observed in the $^{31}P\{^1H\}$ NMR spectrum at – 20.1 ppm, while the ethylene protons appeared as multiplets at 2.46 and 4.07 ppm in the ^1H NMR spectrum. The presence of the CS_2 unit was confirmed by a resonance at 211.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum. A molecular ion in the electrospray mass spectrum (*m/z* 532) and good agreement of determined elemental analysis values with calculated values further supported the formulation of **7** shown in Scheme 2:



Scheme 2. Preparation of the diphosphine bis(dithiocarbamate) ligand **7**.

Nickel bis(dithiocarbamate) complexes represent a reliable and well-established chapter in the library of dithiocarbamate complexes.[2] However, most known $[Ni(S_2CNR_2)_2]$ compounds possess NR_2 units with unreactive substituents. In the project described here, it was not immediately obvious, whether reaction would be limited to the sulfur donors of **7**. Treatment of $NiCl_2{\cdot}6H_2O$ with two equivalents of **6** in methanol led to formation of a green product in good yield. $^{31}P\{^1H\}$ NMR analysis revealed a resonance at – 20.4 ppm (c.f., – 20.4 ppm for **7**), indicating that no reaction had taken place at the phosphines. A shift was observed in the ethylene resonances of 2.34 and 3.56 ppm in the ^1H NMR spectrum relative to the precursor. A displacement of the chemical shift of the CS_2 resonance to 208.7 ppm was noted in the $^{13}C\{^1H\}$ NMR spectrum. On the basis of these data as well as mass spectrometry and elemental analysis results, the product was formulated as $[Ni\{S_2CN(CH_2CH_2PPh_2)_2\}_2]$ (**8**), as shown in Scheme 3. These data agree well with the values recorded for the corresponding amine-terminated literature complex $[Ni\{S_2CN(CH_2CH_2NEt_2)_2\}_2]$.[5]



Scheme 3. Reaction of bifunctional **7** with chloride compounds of group 10.

After the successful reaction of **7** with nickel(II) chloride, it was expected that the same reaction pathway would be followed on treatment of **7** with $[PdCl_2(py)_2]$, as has been observed in the formation of the amino-derivative, $[Pd\{S_2CN(CH_2CH_2NEt_2)_2\}_2]$.[4f] The reaction of **7** and $[PdCl_2(py)_2]$ in a 2:1 ratio yielded a yellow product in mediocre yield. The most informative technique was again $^{31}P\{^1H\}$ NMR spectroscopy, which revealed a change of more than 28 ppm in the chemical shift values of the phosphorus nuclei to 8.2 ppm. The resonances for the CH_2 bridges were found to be split into four separate resonances of equal intensity in the ^1H NMR spectrum between 3.15 and 4.94 ppm. Mass spectrometry data were not particularly diagnostic, however, elemental analysis was consistent for a 1:1 metal:ligand complex rather than in a ratio of 1:2. Slow evaporation of a solution of the complex in methanol yielded single crystals suitable for X-ray diffraction. The structure was determined to reveal a cyclic formulation, $[Pd\{S_2CN(CH_2CH_2PPh_2)_2\}]_2(Cl)_2$ (**9**), as shown in Fig. 3:

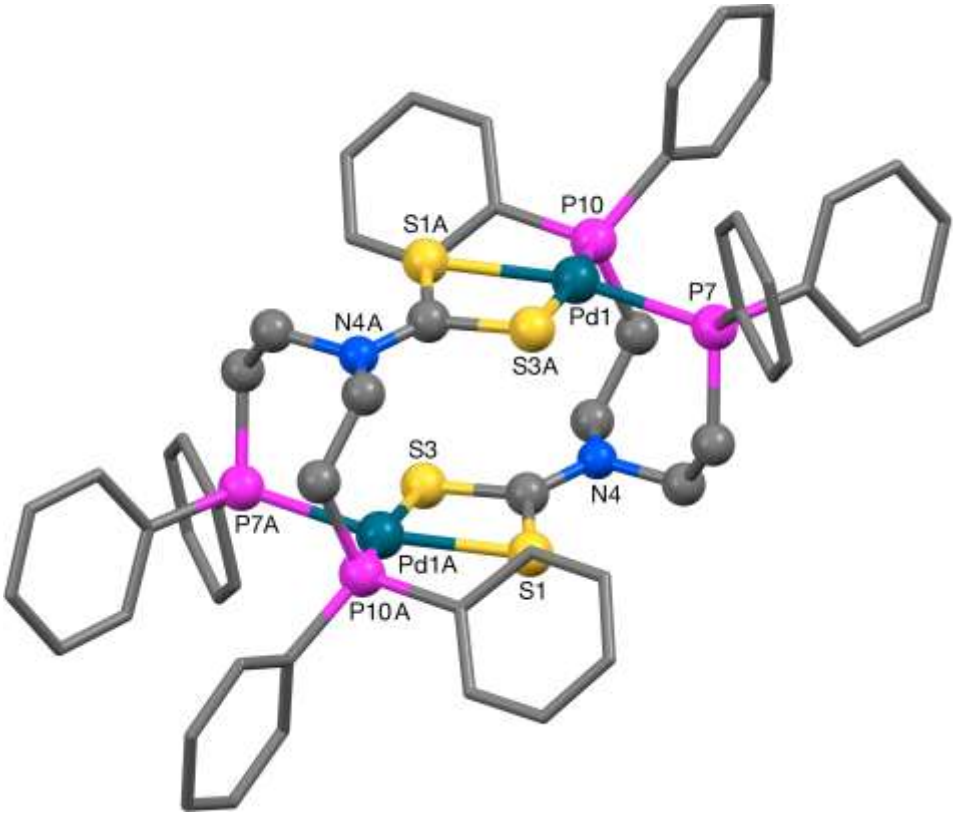


Figure 3. The molecular structure of $[Pd\{S_2CN(CH_2CH_2PPh_2)_2\}]_2(Cl)_2$ (**9**) with the counteranions omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–P(10) = 2.2702(10), Pd(1)–P(7) = 2.2978(11), Pd(1)–S(1A) = 2.3371(10), Pd(1)–S(3A) = 2.3438(10), S(1)–C(2) = 1.714(4), S(1)–Pd(1A) = 2.3372(10), C(2)–N(4) = 1.327(5), C(2)–S(3) = 1.725(4), S(3)–Pd(1A) = 2.3438(10), P(10)–Pd(1)–P(7) = 97.21(4), P(10)–Pd(1)–S(1A) = 95.97(4), P(7)–Pd(1)–S(3A) = 91.02(4), S(1A)–Pd(1)–S(3A) = 74.99(3), S(1)–C(2)–S(3) = 111.9(2).

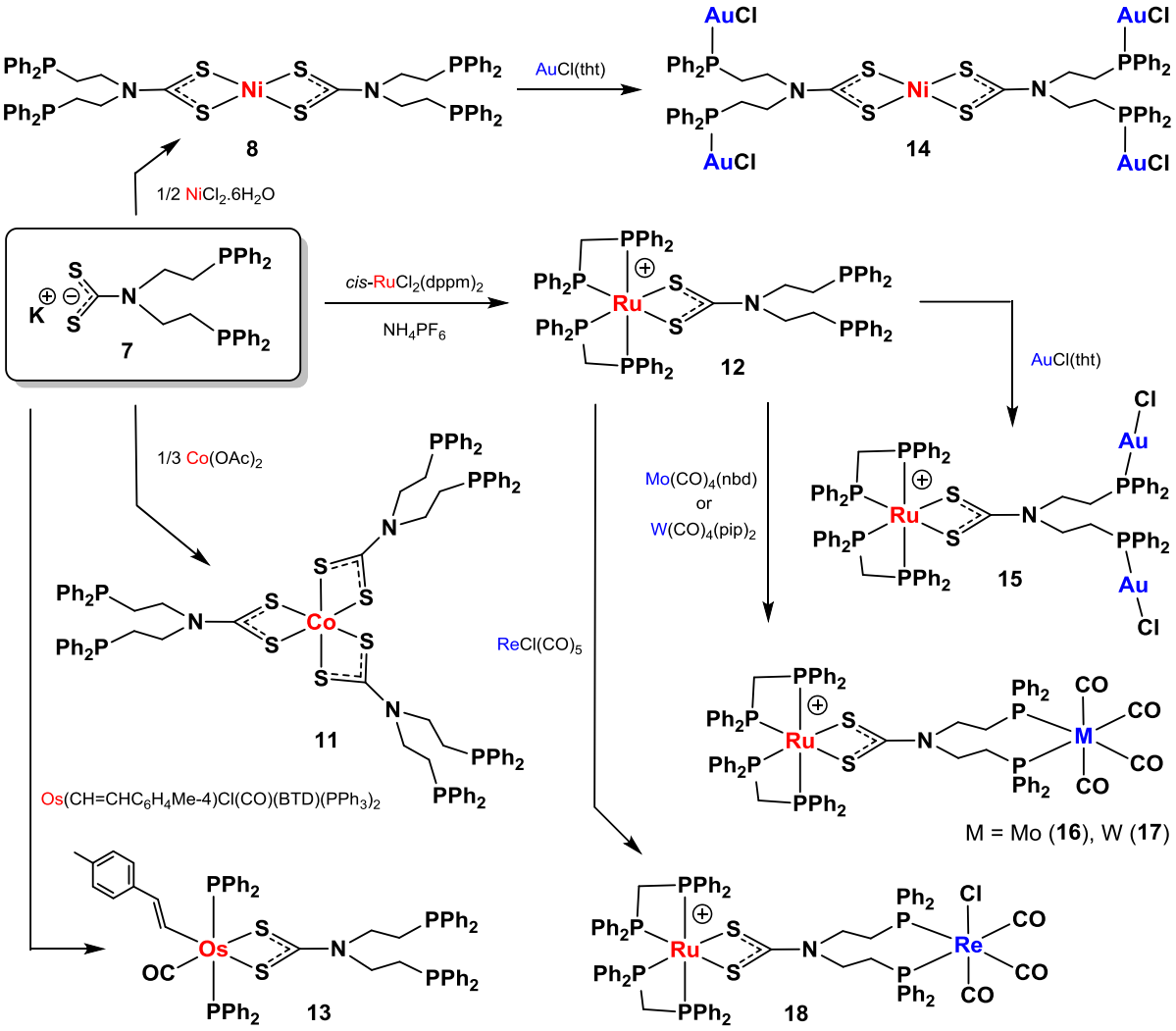
The structural study revealed a square planar arrangement for the bimetallic complex $[Pd\{S_2CN(CH_2CH_2PPh_2)_2\}]_2$ (**9**) in which the two palladium centers are incorporated in a 14-membered ring. The sum of the bond angles around the palladium centers is 359.2°, indicating a relatively low level of distortion from an ideal square planar geometry. The *cis*-interligand angles are 74.99(3) – 97.21(4)° with the smallest angle being the S(1A)–Pd(1)–S(3A) angle and the largest that between the two phosphines. This angle and the bond lengths, Pd(1)–S(1A) [2.3371(10) Å] and Pd(1)–S(3A) [2.3438(10) Å] are similar to comparable palladium dithiocarbamate compounds, such as $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)Pd(PPh_3)_2](BF_4)_2$.[4d] The C(2)–N(4) bond distance of 1.327(5)

Å is clearly multiple in nature, falling between typical distances for C–N and C=N lengths of 1.47 and 1.29 Å, respectively.[20]

The synthesis of **9** was optimized from $[PdCl_2(py)_2]$ using only one equivalent of ligand **7**. The same product was also obtained on attempts to add '$PdCl_2$' units to **8** through reaction with $[PdCl_2(py)_2]$.

This fascinating departure from the reactivity shown with nickel(II) chloride led to the same reaction being investigated with the platinum(II) chloride precursor, $[PtCl_2(NCPh)_2]$. This reaction resulted in the formation of an insoluble yellow precipitate. Denied the possibility of NMR analysis, the formulation of the product rested principally on infrared spectroscopy, which confirmed the presence of the $[S_2CN(CH_2CH_2PPh_2)_2]^-$ ligand, while elemental analysis suggested the ratio of 1:1 for the metal:ligand relationship. On the basis of these data and the insoluble nature of the product, it was formulated as the polymer, $[Pt\{S_2CN(CH_2CH_2PPh_2)_2\}]_n$ (**10**).

In order to explore further geometries beyond 4-coordinate square planar arrangements, the reaction between $[Co(OAc)_2]$ and three equivalents of **7** was investigated. Despite the use of a cobalt(II) precursor, oxidation to the trivalent product is universally observed in dithiocarbamate complexes of the type, $[Co(S_2CNR_2)_3]$.[2d] Coordination solely through the sulfur donors of the ligand was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy, while the ethylene bridges appeared as broad multiplets in the ^1H NMR spectrum between 1.9 and 4.1 ppm. The formulation of the product was confirmed as $[Co\{S_2CN(CH_2CH_2PPh_2)_2\}_3]$ (**11**) on the basis of an $[M+Na]^+$ ion at *m/z* 1630 in the mass spectrum (ES, +ve mode) and good agreement of elemental analysis between determined and calculated values (Scheme 4).



Scheme 4. Reaction to form mono-, di-, tri- and pentametallic compounds (tht = tetrahydrothiophene, pip = piperidine, nbd = norbornadiene).

Once the reactivity of the bifunctional linker **7** had been explored to prepare homoleptic examples, the pendant phosphine groups were explored as a starting point for the generation of multimetallic compounds. Of the group 10 homoleptic compounds reported here, only **8** was found to display pendant phosphines.

In order to expand precursor options, the complex, $[Ru\{S_2CN(CH_2CH_2PPh_2)_2\}(dppm)_2]PF_6$ (**12**), was prepared from the versatile starting material, *cis*-$[RuCl_2(dppm)_2]$. The retention of the coordinated dppm ligands was confirmed by resonances in the $^{31}P\{^1H\}$ NMR spectrum at – 18.6 and 5.6 ppm showing mutual coupling of 34.4 Hz, while the presence of the pendant phosphines was indicated by a singlet at – 21.5 ppm.

The chelation of the dppm ligands in **12** afforded protection against further reaction of the pendant phosphine units with the metal center. However, the need for this precaution was probed using the triphenylphosphine vinyl complex [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$], which has been shown to readily react with dithiocarbamates[4c,6a,b] and be susceptible to loss of phosphines.[21] Reaction of **7** with the ruthenium vinyl precursor on an NMR scale led to relatively rapid substitution (within an hour in solution) of a PPh$_3$ ligand and a mixture of products, possibly oligomeric in nature. However, the osmium analogue, [Os(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$][22] possesses stronger M-P bonds and was considered likely to be more resistant to phosphine loss. The reaction between this compound and **7** led to the formation of [Os(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$PPh$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**13**), which was isolated rapidly before further reaction could occur (Scheme 4). A new singlet resonance was observed in the ^{31}P{^{1}H} NMR spectrum at 7.8 ppm alongside the resonances of the pendant phosphine units at –20.4 and –21.3 ppm. These environments were rendered inequivalent by the lower symmetry of the complex compared to **12**. Retention of the vinyl ligand was indicated by typical features, such as multiplets for the Hα (dt) and Hβ (d) protons at 8.37 and 5.51 ppm, respectively. Mass spectrometry and elemental analysis data confirmed the overall composition of the compound.

Synthesis of heteronuclear complexes

Treatment of **8** with four equivalents of [AuCl(tht)] (tht = tetrahydrothiophene) led to displacement of the thiacycle to form the yellow-green pentametallic compound, [Ni{S$_2$CN(CH$_2$CH$_2$PPh$_2$AuCl)$_2$}$_2$] (**14**) in moderate yield (Scheme 4). A dramatic shift of the singlet resonance in the ^{31}P{^{1}H} NMR spectrum by over 40 ppm from the precursor value to 23.9 ppm indicated that metallation of the phosphorus donors had been achieved. Relatively little change was observed in the ^{1}H nuclear magnetic resonances of the ethylene bridges. An abundant ion corresponding to loss of one chloride ([M-Cl]$^+$) was found at *m/z* 1985 in the electrospray mass spectrum (+ve mode).

Addition of [AuCl(tht)] to **12** also yielded the aurated product, [Ru{S$_2$CN(CH$_2$CH$_2$PPh$_2$AuCl)$_2$}(dppm)$_2$]PF$_6$ (**15**), which was characterized on the basis of multinuclear NMR and infrared spectroscopy as well as analytical data. Compound **12** was

used as a starting point for the addition of metals from groups 6 and 7 of the periodic table. Treatment of **12** with $[Mo(CO)_4(pip)_2]$ or $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) under nitrogen provided $[(dppm)_2Ru\{S_2CN(CH_2CH_2PPh_2)_2\}Mo(CO)_4]PF_6$ (**16**) in moderate yield. A significant shift in the resonance for the pendant phosphines in the $^{31}P\{^1H\}$ NMR to 31.2 ppm was observed and new activity was observed in the solid state infrared spectrum in the typical region for carbonyl absorptions (2018 – 1874 cm^{-1}). In the electrospray mass spectrum (+ve mode), a molecular ion was seen at *m/z* 1594 confirming the overall composition of the compound. The tungsten analogue, $[(dppm)_2Ru\{S_2CN(CH_2CH_2PPh_2)_2\}W(CO)_4]PF_6$ (**17**) was prepared in the same way, though requiring longer stirring (17 h) to achieve full reaction (Scheme 4). This yellow complex was found to show similar spectroscopic features to the molybdenum compound apart from the presence of tungsten satellites (J_{WP} = 244.0 Hz) associated with the singlet resonance at 17.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

Due to the difficulty in isolating $[Mo\{\kappa^2\text{-}HN(CH_2CH_2PPh_2)_2\}(CO)_4]$ (**4**) before spontaneous coordination of the nitrogen donor to the metal, the reactivity of the nitrogen donor towards carbon disulfide could not be investigated. However, the tungsten analogue (**6**) does not undergo the bidentate to tridentate transformation, even after many hours in solution. Accordingly, an alternative route to **17** was attempted through sequential treatment of **6** with K_2CO_3, CS_2 and *cis*-$[RuCl_2(dppm)_2]$. Although this did yield **17** in modest yield, additional products were also obtained. This is possibly due to the dithiocarbamate generated coordinating to unreacted **6**. Zerovalent dithiocarbamate examples $[W(S_2CNR_2)(CO)_4]^-$ are known.[23]

Stirring **12** with $[ReCl(CO)_5]$ under nitrogen led to the formation of $[(dppm)_2Ru\{S_2CN(CH_2CH_2PPh_2)_2\}ReCl(CO)_3]PF_6$ (**18**) in 83% yield to provide a heterobimetallic example combining metals from groups 7 and 8 of the transition series. The presence of the rhenium unit was indicated by the presence of new absorptions in the solid state infrared spectrum between 2036 and 1960 cm^{-1}, while a new singlet was observed at 31.7 ppm in the ^{31}P NMR spectrum.

Conclusions

The new bifunctional diphosphine-dithiocarbamate 'Janus' ligand, $KS_2CN(CH_2CH_2PPh_2)_2$ (**1**), has been prepared in good yield in only two steps from

commercially available bis(2-chloroethyl)amine. Ligand **1** reacts preferentially through the sulfur donors to yield nickel, ruthenium, cobalt and osmium complexes with pendant phosphines, which were then used to synthesise bi-, tri- and pentametallic complexes incorporating the metals Mo, W, Re, Ru, Ni, Pd, Pt, Au. While this reactivity was well controlled in heteroleptic assemblies, allowing multimetallic complexes to be constructed in a stepwise manner (e.g., **8**). However, for homoleptic arrangements, cyclic (**9**) or polymeric (**10**) examples were observed. This reactivity shows the potential for **7** in the stepwise construction of multimetallic assemblies but also illustrates the pitfalls which exist when using such bifunctional linkers.

Experimental Section

General Comments. Unless otherwise stated, all experiments were carried out in air. The complexes obtained appear stable towards the atmosphere, whether in solution or in the solid state. Reagents and solvents were used as received from commercial sources. Petroleum ether is the fraction boiling in the 40–60 °C range. The following complexes were prepared as described elsewhere: $[PdCl_2(py)_2]$,[24] $[PtCl_2(NCPh)_2]$,[25] *cis*-$[RuCl_2(dppm)_2]$,[26] [AuCl(tht)],[27] $[M(CO)_4(pip)_2]$ (M = Mo, W)[28] and $[Mo(CO)_4(nbd)]$.[29] Electrospray (ES) and Fast Atom Bombardment (FAB) mass data were obtained using Micromass LCT Premier and Autospec Q instruments, respectively. 3-Nitrobenzylalcohol (nba) was used as a matrix in some measurements. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer and characteristic triphenylphosphine-associated infrared data are not reported. NMR spectroscopy was performed at 25 °C using Varian Mercury 300 and Bruker AV400 spectrometers in $CDCl_3$ unless stated otherwise. All coupling constants are in Hertz. Resonances in the $^{31}P\{^1H\}$ NMR spectra due to the hexafluorophosphate counteranion were observed where the formulation indicates but are not included below. Elemental analysis data were obtained from London Metropolitan University. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes.

$[Mo\{\kappa^2\text{-}HN(CH_2CH_2PPh_2)_2\}(CO)_4]$ (4)

$[Mo(CO)_4(pip)_2]$ (15 mg, 0.040 mmol) and $[H_2N(CH_2CH_2PPh_2)_2]Cl$ (19 mg, 0.040 mmol) were dissolved in dichloromethane (10 mL) and methanol (5 mL) and stirred for 10 minutes.

The solvent was removed and diethyl ether (10 mL) added. Ultrasonic trituration yielded a yellow-brown product, which was washed with diethyl ether (10 mL) and dried. Yield: 16 mg (62 %). IR (solid state): 2950, 2803, 2734, 2013 ν(CO), 1906 ν(CO), 1887 ν(CO), 1862 ν(CO), 1821, 1790, 1592, 1459, 1433, 1307, 1028, 827, 739, 692 cm^{-1}. NMR ^{1}H: δ 1.66 (m, 4H, PCH_2), 2.71 (m, 4H, NCH_2), 4.25 (s(br), 1H, NH), 7.19 – 7.58 (m, 20H, PPh_2). $^{31}P\{^{1}H\}$: δ 19.8 (s, PPh_2) ppm. MS (ESI +ve) *m/z* (abundance %): 650 (11) $[M]^+$. Analysis: Could not be obtained due to the spontaneous loss of carbon monoxide from the complex.

[Mo{κ^3-HN($CH_2CH_2PPh_2$)$_2$}$(CO)_3$] (5)

$[Mo(CO)_4(pip)_2]$ (25 mg, 0.066 mmol) and $[H_2N(CH_2CH_2PPh_2)_2]Cl$ (32 mg, 0.067 mmol) were dissolved in degassed dichloromethane (10 mL) and stirred at reflux under nitrogen for three hours. Methanol (10 mL) was added and the solvent volume reduced until precipitation of a yellow solid was complete. This was washed with methanol (10 mL) and diethyl ether (10 mL) and dried. Yield: 33 mg (81 %). IR (solid state): 3290, 3240, 1911 ν(CO), 1816 ν(CO), 1793 ν(CO), 638 cm^{-1}. NMR ^{1}H: δ 2.32, 2.44 (m x 2, 4H, PCH_2), 2.91, 3.12 (m x 2, 4H, NCH_2), 4.15 (s(br), 1H, NH), 6.91, 7.13, 7.39, 7.77 (m x 4, 20H, PPh_2). $^{31}P\{^{1}H\}$: δ 39.2 (s, PPh_2) ppm. MS (ESI +ve) *m/z* (abundance %): 622 (20) $[M]^+$. Analysis: Calculated for $C_{31}H_{29}MoNO_3P_2$: C, 59.9; H, 4.7; N, 2.3 %. Found: C, 60.2; H, 4.8; N, 2.1%.

[W{κ^2-HN($CH_2CH_2PPh_2$)$_2$}$(CO)_4$] (6)

$[W(CO)_4(pip)_2]$ (60 mg, 0.129 mmol) and $[H_2N(CH_2CH_2PPh_2)_2]Cl$ (62 mg, 0.130) were dissolved in degassed dichloromethane (20 mL) and stirred at reflux under nitrogen for 21 hours. The resulting solution was filtered through Celite and then methanol (20 mL) added. The solvent volume was reduced to approximately 5 mL and the solution stored at –20 C until precipitation of a pale yellow solid was complete. This was washed with cold methanol (5 mL) and diethyl ether (10 mL) and dried. Yield: 70 mg (74 %). IR (solid state): 3059, 2959, 2817, 2008 ν(CO), 1899 ν(CO), 1874 ν(CO), 1850 ν(CO), 1433, 1280,1090, 913, 799, 740, 690 cm^{-1}. NMR ^{1}H: δ 2.48 (m, 4H, PCH_2), 2.72 (m, 4H, NCH_2), 3.77 (s(br), 1H, NH), 7.36 – 7.54 (m, 20H, PPh_2). $^{31}P\{^{1}H\}$: δ 2.9 (s, PPh_2, J_{PW} = 234.0 Hz) ppm. MS (ESI +ve) *m/z* (abundance %): 738 (100) $[M]^+$. Analysis: Calculated for $C_{32}H_{29}NO_4P_2W{\cdot}CH_2Cl_2$: C, 48.2; H, 3.8; N, 1.7 %. Found: C, 48.3; H, 4.1; N, 1.9%.

$KS_2CN(CH_2CH_2PPh_2)_2$ (7)

A mixture of bis[2-(diphenylphosphino)ethyl]amine hydrochloride (1.00 g, 2.10 mmol) and potassium carbonate (2.31 g, 16.75 mmol) in dry, degassed acetonitrile (25 mL) was treated with carbon disulfide (0.127 mL, 2.09 mmol). The resultant mixture was stirred at room temperature for 1 h. The pale yellow solution was filtered and all solvent removed under reduced pressure. The crude solid was dissolved in the minimum amount of dichloromethane and filtered through Celite. All solvent was removed under reduced pressure to yield the product as a yellow foamy solid which was dried under vacuum overnight. Yield: 1.06 g (91 %). IR (solid state): 3054, 2903, 1478, 1432, 997, 731, 692 cm^{-1}. NMR ^{1}H: δ 2.47 (m, 4H, PCH_2), 4.10 (m, 4H, NCH_2), 7.26, 7.42 (m x 2, 20H, PPh_2) ppm. $^{13}C\{^{1}H\}$: δ 211.5 (CS_2), 138.1 (d, *ipso*-C_6H_5, J_{CP} = 12.0 Hz), 132.8 (d, *o*-C_6H_5, J_{CP} = 18.6 Hz), 128.6 (s, *p*-C_6H_5), 128.5 (d, *m*-C_6H_5, J_{CP} = 6.7 Hz), 51.0 (d, PCH_2, J_{CP} = 25.4 Hz), 25.7 (d, NCH_2, J_{CP} = 14.0 Hz) ppm. $^{31}P\{^{1}H\}$: δ – 20.1 (s, PPh_2) ppm. MS (ESI –ve) *m/z* (abundance %): 532 (100) $[M+H_2O]^-$. Analysis: Calculated for $C_{29}H_{28}KNP_2S_2$: C, 62.7; H, 5.1; N, 2.5%. Found: C, 63.0; H, 5.2; N, 2.4%.

$[Ni\{S_2CN(CH_2CH_2PPh_2)_2\}_2]$ (8)

A solution of $NiCl_2 \cdot 6H_2O$ (21.2 mg, 0.090 mmol) in degassed methanol (2 mL) was added to a solution of **7** (100 mg, 0.180 mmol) in degassed methanol (4 mL) and the reaction stirred at room temperature for 2 h leading to the formation of a green precipitate. All solvent was removed under reduced pressure and the solid dissolved in the minimum amount of dichloromethane and filtered through Celite. The solution was concentrated to approximately 2 mL and methanol (10 mL) added. The flask was kept at – 20 °C overnight and the resulting green product was filtered, washed with methanol (10 mL) and hexane (2 x 5 mL) and dried under vacuum. Yield: 70 mg (71 %). IR (solid state): 3048, 2913, 1480, 1432, 998, 737, 694 cm^{-1}. NMR ^{1}H: δ 2.34 (m, 8H, PCH_2), 3.56 (m, 8H, NCH_2), 7.24 – 7.50 (m, 40H, PPh_2). $^{13}C\{^{1}H\}$: δ 206.9 (CS_2), 136.8 (d, *ipso*-C_6H_5, J_{CP} = 10.6 Hz), 132.6 (d, *o*-C_6H_5, J_{CP} = 17.5 Hz), 129.4 (s, *p*-C_6H_5), 128.7 (s(br), *m*-C_6H_5), 47.0 (d, PCH_2, J_{CP} = 20.4 Hz), 25.9 (d, NCH_2, J_{CP} = 14.8 Hz) ppm. $^{31}P\{^{1}H\}$: δ – 20.4 (s, PPh_2) ppm. MS (ES +ve) *m/z* (abundance %): 1322 (21) $[M+2K+nba]^+$. Analysis: Calculated for $C_{58}H_{56}N_2NiP_4S_4$: C, 63.8; H, 5.2; N, 2.6%. Found: C, 63.6; H, 5.3; N, 2.5%.

$[Pd\{S_2CN(CH_2CH_2PPh_2)_2\}]_2(Cl)_2$ (9)

$[PdCl_2(py)_2]$ (70 mg, 0.210 mmol) was added to a solution of **7** (116 mg, 0.209 mmol) in dry, degassed dichloromethane (15 mL). The yellow mixture was stirred at reflux under N_2 for 2 hours. The resulting yellow precipitate was filtered, dissolved in methanol and filtered through Celite. All solvent was then removed under reduced pressure and the resulting yellow solid was washed with dichloromethane and acetone before drying under vacuum. Yield: 195 mg (71 %). IR (solid state): 3049, 2903, 1496, 1483, 1432, (PPh_2), 1132, 1125, 890 cm^{-1}. NMR ^1H (methanol-d^4): δ 3.15, 3.58 (m x 2, 8H, PC*H*$_2$CH$_2$N), 4.32, 4.94 (m x 2, 8H, PC*H*$_2$CH$_2$N), 7.57 – 7.16 (m, PPh_2, 40H) ppm. $^{31}P\{^1H\}$ (methanol-d^4): δ 8.2 (s, PPh_2) ppm. MS (ESI +ve) *m/z* (abundance %): 1245 (5) $[M]^+$. Analysis: Calculated for $C_{58}H_{56}Cl_2N_2P_4Pd_2S_4$: C, 52.9; H, 4.3; N, 2.1%. Found: C, 52.8; H, 4.0; N, 2.2%.

$\{[Pt\{S_2CN(CH_2CH_2PPh_2)_2\}]Cl\}_n$ (10)

$[PtCl_2(NCPh)_2]$ (25 mg, 0.053 mmol) in degassed dichloromethane (3 mL) was added to a solution of **7** (29 mg, 0.052 mmol) in degassed dichloromethane (3 mL) and stirred at room temperature for 1 h. The yellow precipitate formed was filtered, washed with dichloromethane (10 mL) and acetone (10 mL) and dried under vacuum. Yield: 32 mg, (81 %). IR (solid state): 1506, 1498, 1434, 1390, 1323, 1187, 1098, 1028, 998, 930, 810, 740, 690 cm^{-1}. MS (ESI +ve) *m/z* (abundance %): 1543 (6) $[2M+3K]^+$. Analysis: Calculated for $C_{29}H_{28}ClNP_2PtS_2 \cdot 2CH_2Cl_2$: C, 40.6; H, 3.5; N, 1.5%. Found: C, 40.5; H, 3.3; N, 1.7%.

$[Co\{S_2CN(CH_2CH_2PPh_2)_2\}_3]$ (11)

A solution of ligand **7** (100 mg, 0.180 mmol) and $[Co(OAc)_2] \cdot 4H_2O$ (15 mg, 0.060 mmol) in degassed methanol (3 mL) was stirred at room temperature for 2 h. All solvent was removed under reduced pressure and the resulting residue dissolved in a minimum volume of dichloromethane and filtered through Celite. The solution was concentrated to approximately 2 mL and pentane (10 mL) added to precipitate the dark brown product, which was dried under vacuum. Yield: 66 mg (68 %). IR (solid state): 3039, 1478, 1431, 999, 735, 692 cm^{-1}. NMR ^1H: δ 1.9 – 4.1 (m(br), 24H, CH_2), 7.06 – 7.84 (m, 60 H, PPh_2) ppm. $^{31}P\{^1H\}$: δ –20.4 (s, PPh_2) ppm. MS (ESI +ve) *m/z* (abundance %): 1630 (20) $[M+Na]^+$. Analysis: Calculated for $C_{87}H_{84}CoN_3P_6S_6$: C, 65.0; H, 5.3; N, 2.6%. Found: C, 65.3; H, 5,2; N, 2.7%.

[Ru{$S_2CN(CH_2CH_2PPh_2)_2$}$(dppm)_2$]PF_6 (12)

A yellow solution of ligand **7** (50 mg, 0.090 mmol) and *cis*-[$RuCl_2(dppm)_2$] (83.4 mg, 0.089 mmol) in degassed dichloromethane (20 mL) was treated with a solution of ammonium hexafluorophosphate (29 mg, 0.178 mmol) in degassed methanol (10 mL). The solution was heated at reflux for 10 minutes followed by stirring at room temperature for 4 h. All solvent was removed under reduced pressure to yield the yellow crude product, which was dissolved in a minimum volume of dichloromethane and filtered through Celite to remove KCl. All solvent was again removed before ultrasonic trituration in diethyl ether (25 mL). The yellow product was washed with diethyl ether (10 mL), then filtered and dried under vacuum. Yield: 85 mg (62 %). IR (solid state): 1748, 1484, 1435, 1370, 1292, 1188, 1098, 1000, 836 (ν_{PF}), 695 cm^{-1}. NMR ^1H: δ 1.97, 2.16 (m x 2, 4H, PC$H_2$$CH_2$N), 3.31, 3.78 (m x 2, 4H, PCH_2CH_2N), 4.61, 4.93 (m x 2, 4H, PCH_2P), 6.50 (m, 4H, C_6H_5-dppm), 6.96 – 7.10, 7.19 – 7.66, (m x 2, 56H, C_6H_5) ppm. $^{31}P\{^1H\}$ (CD_2Cl_2): δ –21.3 (s, PPh_2), –18.6, –5.7 (pseudotriplet x 2, dppm, J_{PP} = 34.4 Hz) ppm. MS (MALDI +ve) *m/z* (abundance %) 1422 (100) $[M + 2H_2O]^+$. Analysis: Calculated for $C_{79}H_{72}F_6NP_7RuS_2$: C, 62.0; H, 4.7; N, 0.9 %. Found: C, 61.8; H, 4.6; N, 1.0%.

[Os(CH=CHC_6H_4Me-4){$S_2CN(CH_2CH_2PPh_2)_2$}(CO)$(PPh_3)_2$] (13)

Ligand **7** (25 mg, 0.045 mmol) and [Os(CH=CHC_6H_4Me-4)Cl(CO)(BTD)$(PPh_3)_2$] (45 mg, 0.044 mmol) were dissolved in dichloromethane (5 mL) and stirred at room temperature for 1 minute. The solution was filtered through Celite and all solvent then removed. Petroleum ether (10 mL) was added and a cream solid was obtained by trituration in an ultrasound bath. The product was filtered and washed with petroleum ether (10 mL) and dried under vacuum. Yield: 28 mg (46 %). IR (solid state): 1901 (ν_{CO}), 1573, 1547, 1507, 1481, 1433, 1348, 1278, 1186, 1158, 1116, 1091, 999, 848, 740, 692 cm^{-1}. NMR ^1H: δ 1.70, 1.91 (m x 2, 4H, PC$H_2$$CH_2$N), 2.21 (s, 3H, Me), 2.71, 3.12 (m x 2, 4H, PCH_2CH_2N), 5.51 (d, 1H, Hβ, J_{HH} = 17.1 Hz), 6.47, 6.83 (AB, 4H, C_6H_4, J_{AB} = 8.0 Hz), 6.92 – 7.53 (m, 50H, C_6H_5), 8.37 (dt, 1H, Hα, J_{HH} = 17.1 Hz, J_{HP} = 2.2 Hz) ppm. $^{31}P\{^1H\}$ (CD_2Cl_2): δ –21.3, –20.4 (s x 2, PPh_2), 7.8 (s, $OsPPh_3$) ppm. MS (ES +ve) *m/z* (abundance %) 1412 (3) $[M + 2H_2O]^+$. Analysis: Calculated for $C_{75}H_{67}NOOsP_4S_2$: C, 65.4; H, 4.9; N, 1.0 %. Found: C, 65.6; H, 5.0; N, 1.0%.

[Ni{$S_2CN(CH_2CH_2PPh_2AuCl)_2$}$_2$] (14)

A solution of [AuCl(tht)] (200 mg, 0.624 mmol) in degassed dichloromethane (5 mL) was added dropwise to a solution of **8** (150 mg, 0.137 mmol) in degassed dichloromethane (5 mL) and the resulting solution was stirred at room temperature for 1 h. Under reduced pressure, the solvent volume was concentrated to approximately 2 mL and diethyl ether (10 mL) added leading to the precipitation of a yellow solid. The solid was left to settle at –20 °C overnight then filtered and dried under vacuum. Yield: 200 mg (72 %). IR (solid state): 1751, 1482, 1436, 1410, 1353, 1285, 1177, 1104, 998, 742, 690 cm^{-1}. NMR ^1H (CD_2Cl_2): δ 3.03 (m, 8H, CH_2), 3.93 (m, 8H, CH_2), 7.50, 7.69 (m x 2, 40 H, PPh_2) ppm. $^{31}P\{^1H\}$ (CD_2Cl_2): δ 23.9 (s, PPh_2) ppm. MS (LSIMS +ve) *m/z* (abundance %) 1983 (30) $[M\text{-}Cl]^+$. Analysis: Calculated for $C_{58}H_{56}Au_4Cl_4N_2NiP_4S_4$: C, 34.5; H, 2.8; N, 1.4%. Found: C, 34.9; H, 3.0; N, 1.5%.

[Ru{$S_2CN(CH_2CH_2PPh_2AuCl)_2$}(dppm)$_2$]$PF_6$ (15)

A solution of [AuCl(tht)] (42 mg, 0.131 mmol) in degassed dichloromethane (3 mL) was added drop wise to a solution of **12** (100 mg, 0.065 mmol) in degassed dichloromethane (3 mL) and the resulting solution was stirred at room temperature for 1 h. All solvent was removed under reduced pressure and the resulting precipitate dissolved in the minimum amount of dichloromethane and filtered through Celite. The solution was concentrated to approximately 2 mL and diethyl ether (5 mL) added causing a yellow solid to precipitate. The product was filtered and dried under vacuum. Yield: 100 mg (77 %). IR (solid state): 1737, 1484, 1436, 1365, 1189, 1102, 999, 836 (ν_{PF}), 739, 691 cm^{-1}. NMR ^1H (CD_2Cl_2): δ 2.33, 2.53 (m x 2, 4H, PC$H_2$$CH_2$N), 4.17, 4.44 (m x 2, 4H, $PCH_2C$$H_2$N), 4.44, 4.86 (m x 2, 4H, PCH_2P), 6.41 (m, 4H, C_6H_5-dppm), 6.93 – 7.78 (m, 56H, C_6H_5) ppm. $^{31}P\{^1H\}$ (CD_2Cl_2): δ – 17.4, – 6.0 (pseudotriplet x 2, dppm, J_{PP} = 34.4 Hz), 25.4 (s, $AuPPh_2$) ppm. MS (MALDI +ve) *m/z* (abundance %) 1853 (28) $[M]^+$. Analysis: Calculated for $C_{79}H_{72}Au_2Cl_2F_6NP_7RuS_2 \cdot 4CH_2Cl_2$ C, 42.7; H, 3.5; N, 0.6%. Found: C, 42.7; H, 3.4; N, 0.9%.

[(dppm)$_2$Ru{$S_2CN(CH_2CH_2PPh_2)_2$}Mo(CO)$_4$]PF_6 (16)

Compound **12** (80 mg, 0.052 mmol) and [Mo(CO)$_4$(nbd)] (18 mg, 0.057 mmol) were dissolved in degassed dichloromethane (15 mL) and stirred at room temperature for 2 h under nitrogen. The solution was filtered through Celite and all solvent then removed. Petroleum ether (20 mL) was added and an orange solid was obtained by trituration in an ultrasound

bath. The product was filtered and washed with petroleum ether (10 mL) and dried under vacuum. Yield: 63 mg (70 %). IR (solid state): 2018 (ν_{CO}), 1918 (ν_{CO}), 1874 (ν_{CO}), 1605, 1483, 1434, 1317, 1293, 1259, 1243, 1189, 1174, 1163, 1098, 1085, 1063, 1029, 997, 911, 827 (ν_{PF}), 812 cm^{-1}. NMR ^1H (CD_2Cl_2): δ 2.29 (m, 4H, PC*H*$_2$CH$_2$N), 3.51, 3.81 (m x 2, 2H, PCH$_2$C*H*$_2$N), 4.46, 4.92 (m x 2, 4H, PCH$_2$P), 4.94 (m, 2H, PCH$_2$C*H*$_2$N), 6.49 (m, 4H, C_6H_5-dppm), 6.85 – 7.71 (m, 56H, C_6H_5) ppm. $^{31}P\{^1H\}$ (CD_2Cl_2): δ –17.9, –5.4 (pseudotriplet x 2, dppm, J_{PP} = 34.3 Hz), 31.2 (s, MoPPh$_2$) ppm. MS (ES +ve) *m/z* (abundance %) 1594 (62) $[M]^+$. Analysis: Calculated for $C_{83}H_{72}F_6MoNO_4P_7RuS_2$: C, 57.3; H, 4.2; N, 0.8%. Found: C, 57.1; H, 4.3; N, 0.8%.

[(dppm)$_2$Ru{S$_2$CN(CH$_2$CH$_2$PPh$_2$)$_2$}W(CO)$_4$]PF$_6$ (17)

Compound **12** (35 mg, 0.023 mmol) and [W(CO)$_4$(pip)$_2$] (13.4 mg, 0.029 mmol) were dissolved in degassed dichloromethane (8 mL) and stirred at room temperature for 17 h under nitrogen. The solution was filtered through Celite and all solvent was then removed. Petroleum ether (20 mL) was added and a yellow solid was obtained by trituration in an ultrasound bath. The product was filtered and washed with petroleum ether (10 mL) and dried under vacuum. Yield: 29 mg (69 %). IR (solid state): 2008 (ν_{CO}), 1867 (ν_{CO}), 1829 (ν_{CO}), 1358, 1309, 1289, 1261, 1186, 1094, 1026, 1000, 833 (ν_{PF}) cm^{-1}. NMR ^1H (CD_2Cl_2): δ 2.64, 2.53 (m x 2, 4H, PC*H*$_2$CH$_2$N), 3.51 (m, 4H, PCH$_2$C*H*$_2$N), 4.49, 4.87 (m x 2, 4H, PCH$_2$P), 6.49 (m, 4H, C_6H_5-dppm), 6.89 – 7.74 (m, 56H, C_6H_5) ppm. $^{31}P\{^1H\}$ (CD_2Cl_2): δ –18.2, –5.2 (pseudotriplet x 2, dppm, J_{PP} = 33.9 Hz), 17.5 (s, WPPh$_2$, J_{PW} = 244.0 Hz) ppm. MS (ES +ve) *m/z* (abundance %) 1682 (31) $[M]^+$. Analysis: Calculated for $C_{83}H_{72}F_6NO_4P_7RuS_2W{\cdot}CH_2Cl_2$: C, 52.8; H, 3.9; N, 0.7%. Found: C, 53.0; H, 3.5; N, 0.8%.

[(dppm)$_2$Ru{S$_2$CN(CH$_2$CH$_2$PPh$_2$)$_2$}ReCl(CO)$_3$]PF$_6$ (18)

Compound **12** (40 mg, 0.026 mmol) and [ReCl(CO)$_5$] (9.5 mg, 0.026 mmol) were dissolved in degassed dichloromethane (10 mL) and stirred at room temperature for 15 h under nitrogen. The solution was filtered through Celite and all solvent then removed. Petroleum ether (20 mL) was added and a yellow solid was obtained by trituration in an ultrasound bath. The product was filtered and washed with petroleum ether (10 mL) and dried under vacuum. Yield: 50 mg (83 %). IR (solid state): 2036 (ν_{CO}), 1990 (ν_{CO}), 1979 (ν_{CO}), 1960 (ν_{CO}), 1719, 1483, 1434, 1356, 1285, 1184, 1096, 832 (ν_{PF}) cm^{-1}. NMR ^1H: δ 2.38 (m, 4H, PC*H*$_2$CH$_2$N), 3.59, 4.09 (m x 2, 4H, PCH$_2$C*H*$_2$N), 4.64, 5.03 (m x 2, 4H, PCH$_2$P), 6.53 (m, 4H, C_6H_5-

dppm), 6.82 – 7.96 (m, 56H, C_6H_5) ppm. $^{31}P\{^1H\}$: δ – 18.1, – 5.5 (pseudotriplet x 2, dppm, J_{PP} = 33.4 Hz), 31.7 (s, $RePPh_2$) ppm. MS (ES +ve) *m/z* (abundance %) 1692 (8) $[M]^+$. Analysis: Calculated for $C_{82}H_{72}ClF_6NO_3P_7ReRuS_2$: C, 53.6; H, 4.0; N, 0.8%. Found: C, 53.4; H, 3.9; N, 0.8%.

Crystallography

Crystals of **4** were grown by slow diffusion of hexane into a solution of the complex in dichloromethane. Data were taken from this sample on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data reduction and integration was carried out with SAINT+ and absorption corrections applied using the program SADABS. The structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). Structure solution and refinement used the SHELXTL PLUS V6.10 program package.[30]

Crystals of compound **9** were grown by slow evaporation of a solution of the complex in methanol. Data were collected using an Oxford Diffraction Xcalibur 3 diffractometer, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[31]

Crystal data for **5**: $C_{31}H_{29}MoNO_3P_2$, M = 621.43, triclinic, P-1 (no. 2), a = 9.1979(5), b = 9.4053(5), c = 16.4401(9) Å, α = 99.193(1), β = 91.308(1), γ = 100.745(1)°, V = 1377.3(1) $Å^3$, Z = 2, D_c = 1.498 g cm^{-3}, μ(Mo-Kα) = 0.626 mm^{-1}, T = 150 K, yellow blocks, Bruker Smart Apex diffractometer; 6328 independent measured reflections (R_{int} = 0.0124), F^2 refinement,[1] R_1(obs) = 0.0212, wR_2(all) = 0.0541, 6134 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°], 347 parameters. CCDC 1017334.

Crystal data for **9**: $[C_{58}H_{56}N_2P_4Pd_2S_4](Cl)_2 \cdot 2H_2O \cdot 1.5MeOH$, M = 1400.96, monoclinic, $P2_1/n$ (no. 14), a = 11.4321(3), b = 17.1025(5), c = 15.3940(5) Å, β = 100.016(3)°, V = 2963.93(16) $Å^3$, Z = 2 [C_i symmetry], D_c = 1.570 g cm^{-3}, μ(Mo-Kα) = 0.993 mm^{-1}, T = 173

K, yellow blocks, Agilent Xcalibur 3E diffractometer; 6482 independent measured reflections (R_{int} = 0.0604), F^2 refinement,[1] R_1(obs) = 0.0501, wR_2(all) = 0.1077, 4736 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°], 334 parameters. CCDC 1017335.

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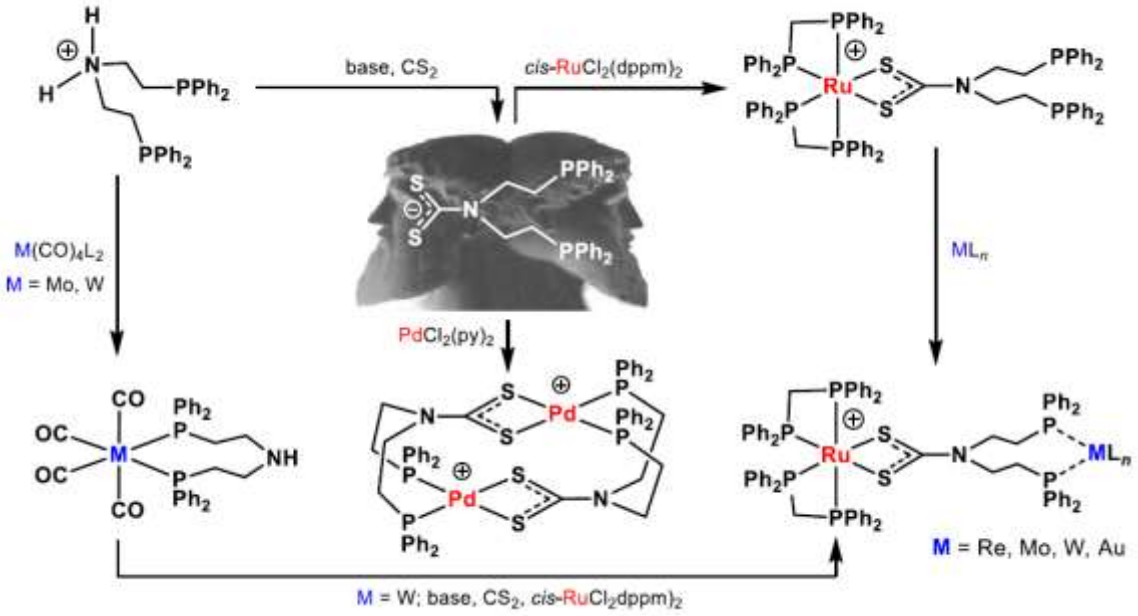
For Table of Contents:

Multimetallic complexes based on a diphosphine-dithiocarbamate 'Janus' ligand.

Rebecca Sherwood, Ferran Gonzàlez de Rivera, Jane Hui Wan, Qi Zhang, Andrew J. P. White, Oriol Rossell, Graeme Hogarth and James D. E. T. Wilton-Ely*



The readily accessible bifunctional phosphine-dithiocarbamate ligand, $KS_2CN(CH_2CH_2PPh_2)_2$ acts as a versatile linker for transition metal units from across groups 7-11 of the periodic table. Diverse reactivity is observed with homoleptic examples, which form mono-, di- or polynuclear compounds depending on the metal employed.